

Synthesis, characterization and *cis*–*trans* influence in cobaloximes with nioxime

B.D. Gupta ^{a,*}, Kushal Qanungo ^a, R. Yamuna ^a, Ashutosh Pandey ^a, Usha Tewari ^a,
V. Vijaikanth ^a, Veena Singh ^a, T. Barclay ^b, W. Cordes ^b

^a Department of Chemistry, I.I.T. Kanpur, UP India, Kanpur 208016, India

^b Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR, USA

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Abstract

A synthetic scheme leading to the (X)(Y)bis(1,2-cyclohexanedionedioximate)cobalt(III) complexes, where X = Cl, N₃, ClCH₂, CH₃, C₂H₅ and Y = PPh₃ and Py is reported. The complexes have been characterized by the usual spectroscopic techniques and have been compared with the reported analogous compounds having other dioximes as the equatorial ligands. The first crystal structure of an inorganic cobaloxime with 1,2-cyclohexanedionedioxime (Nioxime) is reported. For a range of X ligands, a clear trend between ³¹P, ¹³C, ¹H chemical shifts of the equatorial and axial ligands as well as with the Co → chgH charge transfer band has been observed. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Cobaloximes, (X)Co^{III} (dmgH)₂(Y), have extensively been used to mimic the vitamin B₁₂ coenzyme [1–3]. Apart from the structural similarities, the theoretical calculations have shown a close resemblance between the m.o.'s of the cobalamins and cobaloximes [4]. This is reflected in their catalytic abilities for many important organic transformations [5–20].

Cis and *trans* influences, originally defined in square planar platinum(II) systems, described the bond weakening effect one ligand had on others [21]. The study now includes investigations of all possible steric and electronic changes detectable in the *cis* or *trans* ligands. Cobalt(III) complexes [22] and particularly cobaloximes [2,3], due to their ready availability, are the preferred systems for *cis* and *trans* influence studies in octahedral systems. Usually either the axial ligand X or the basal group Y is varied systematically and the changes in the *cis* equatorial dioxime ligand or the *trans* axial ligand is

monitored spectroscopically, or the structural changes are followed from their X-ray structures. UV–vis [4,23,24], IR [25–27], ¹H [28–33], ¹³C [34–40], ³¹P [41,42] and ¹⁹F [43–45] spectroscopy have been used as probes for such studies in cobaloximes. The Co–C bond dissociation energy in organocobaloximes is found to depend on Y [2] and the dissociation constant of Y depends on X [2]. The metal–ligand axial bond and the butterfly bending¹ of the dioxime ligands is found to depend on the steric and electronic properties of the axial ligands [3]. Several attempts have been made to correlate the wealth of information available [23,31,39,46–53].

Most of these studies have involved dmgH as the dioxime ligand in organocobaloximes. The studies involving other oximes with varying steric and electronic properties such as gH [54,55], chgH [56,57] and dpGH [4,58–60] have been few. Recently we have shown that the *cis* influence of the dioxime ligand in alkylcobaloximes varies dpGH > chgH > dmgH [61] and the same order is conserved in organobridged [46] as well as in ligand bridged dicobaloximes [62]. In a separate study,

* Corresponding author. Tel.: +91-512-597730; fax: +91-512-597436.

E-mail address: bdg@iitk.ac.in (B.D. Gupta).

¹ For definition and other details see [3].

Table 1
% yields and analytical data for XCo(chgH)₂Y

Compound number	Y	X	%Yield	R _f (EtOAc)	C	H	N
1a	PPh ₃	Cl	69	0.8	56.2 (56.4)	5.3 (5.2)	8.7 (8.8)
1b	Py	Cl	73	0.8	44.9 (44.8)	5.00 (5.1)	15.4 (15.4)
2a	PPh ₃	N ₃	79	0.7	55.7 (55.8)	5.2 (5.1)	15.1 (15.2)
2b	Py	N ₃	85	0.7	44.1 (44.2)	4.9 (5.0)	24.3 (24.2)
3a	PPh ₃	ClCH ₂	47	0.9	57.0 (57.0)	5.5 (5.4)	8.7 (8.6)
3b	Py	ClCH ₂	70	0.6	46.0 (46.0)	5.3 (5.3)	14.8 (14.9)
4a	PPh ₃	Me	33	0.9	60.2 (60.2)	5.8 (5.9)	9.1 (9.1)
4b	Py	Me	69	0.7	49.6 (49.7)	6.0 (6.0)	16.0 (16.1)
5a	PPh ₃	Et	35	0.8	60.8 (60.8)	6.1 (6.0)	8.8 (8.9)
5b	Py	Et	73	0.8	50.6 (50.8)	6.3 (6.3)	15.2 (15.3)

we have also reported the *trans* influence of the axial ligand [63].

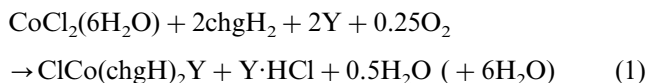
All these studies have involved an alkyl σ donor group as one of the axial ligands. In this paper, we extend our studies to inorganic cobaloximes with σ and π donor ligands. We also address the question of whether the dioxime moiety has any effect on the butterfly bending and on the *cis* and *trans* influence order of the axial ligands.

2. Results and discussion

2.1. Synthesis

The synthesis of XCo(chgH)₂Y (X = Cl, N₃, ClCH₂, Me, Et) Y = PPh₃ (**1a–5a**); Y = Py (**1b–5b**) complexes was accomplished following the well established procedures for the gH [55], dmgH [64], and dpgh [60b,c] complexes.

Refluxing a ethanolic solution of cobalt(II) chloride, chgH₂ and an appropriate base (method 1a) followed by vigorous aeration yields the desired ClCo(chgH)₂Y complex (Eq. (1)).



One equivalent of an inorganic base (NaOH or KOH) can replace an equivalent amount of the appropriate organic base (Py) (methods 1a,b and 2a) without compromising the yield [25].

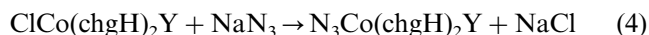
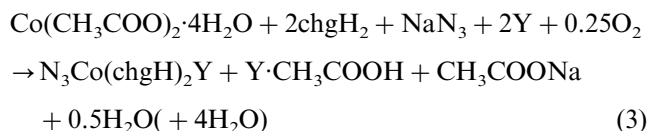
One can achieve the following reaction simply by adding the appropriate base to the aquo complex, (method 1b) (Eq. (2)) formed in situ, from cobalt(II) chloride and chgH₂ in acetone.



For the synthesis of cobaloximes with Y = PPh₃ by a ligand exchange reaction (method 1b), less than the

stoichiometric quantity of triphenylphosphine was used [ClCo(chgH)₂(H₂O)–PPh₃, 1.0/0.60] to avoid the formation of the double complex salt [Co(chgH)₂Cl₂]-[Co(chgH)₂(PPh₃)₂] [65].

Azido complexes were synthesized directly from cobalt acetate and sodium azide (method 2a)(Eq. (3)) or indirectly by substitution of chloride by azide (method 2b)(Eq. (4)) [66].



Organocobaloximes were prepared essentially by the same method reported earlier by us [61]. Yields (%), R_f values (in ethylacetate) and analytical data are tabulated in Table 1.

2.2. Spectroscopy

The spectroscopic characteristics of cobaloximes with dmgH as the equatorial ligand show a systematic variation with X. It is anticipated that a more comprehensive spectroscopic and structural study of a large number of cobaloximes (having different dioximes) with various X ligands (having a range of σ and π donor/acceptor properties) would enable a more rigorous treatment of the statistical data with a greater degree of confidence. The present study, therefore, gains importance as it indicates that the *cis* and *trans* influencing order of the axial ligand X is independent of the equatorial ligand in cobaloximes. The following discussion of the trends in the spectroscopic properties illustrates this point.

The least square method [67] and Microsoft Excel for Windows 95 version 7.0 have been used for the correlation analysis.

Table 2

¹H shifts and Co → dioxH CT band $\lambda_{\max}$ in XCo(chgH)₂Y^{a,b}

Number	Co-(CH ₂)-	Me	Py _α	Py _γ	Py _β	ΔPy _α	ΔPy _γ	ΔPy _β	$\lambda_{\max}$ (log ε)
1a									246 (4.2)
1b			8.26	7.72	7.25	-0.31	0.29	0.20	258 (4.3)
2a									246 (4.3)
2b			8.32	7.74	7.26	-0.25	0.31	0.21	253 (4.2)
3a	3.85								248 (4.3)
3b	3.78		8.58	7.76	7.74	0.01	0.33	0.30	249 (4.4)
4a	0.86								246 (4.2)
4b^c	0.85		8.62	7.73	7.33	0.05	0.30	0.28	247 (4.3)
5a	1.93	0.37							249 (4.4)
5b^c	1.77	0.37	8.60	7.72	7.32	0.03	0.29	0.27	246 (4.3)

^a ¹H of free Py: α = 8.57, β = 7.05 and γ = 7.43.^b All compounds show four sets of multiplet in the range of 2.2–2.5, 3.0–3.1, 1.5–1.6 and 1.7–1.8 due to cyclohexane ring protons.^c Values taken from [61].

Table 3

(a) ³¹P and ¹³C shifts in **1–5a,b** and (b) ¹³C shifts of Pyridine in **1b–5b**

Compound number	³¹ PPh ₃	Δ ³¹ P	C=N	C ^a	C'	C ₁	C ₂
1a	25.32	30.52	153.45	26.07	21.04		
1b			153.62	26.12	23.33		
2a	23.75	28.95	152.65	25.89	21.18		
2b			153.12	25.99	21.45		
3a	20.50	25.70	150.53	25.41	21.23	65.23	
3b			151.12	25.39	21.45		
4a	19.81	25.01	149.24	25.15	21.37		
4b^a			150.04	25.05	21.44	11.56	
5a	20.36	25.56	149.06	25.01	21.29		15.08
5b^a			150.07	25.08	21.60	26.01	15.82
Compound number	¹³ C Py _α	Δ ¹³ CPy _α	¹³ CPy _β	Δ ¹³ Cpy _β	¹³ C Py _γ	Δ ¹³ CPy _γ	
1b	151.09	1.27	125.66	1.93	138.96	3.07	
2b	151.30	1.48	125.7	1.97	138.80	2.91	
3b	150.28	0.46	125.40	1.67	137.91	2.02	
4b^a	149.89	0.07	125.09	1.36	137.38	1.49	
5b^a	149.89	0.07	125.02	1.29	137.25	1.36	

^a ¹³C shift of Free Py: α = 149.82, β = 123.73 and γ = 135.89.

2.3. Cis and trans influence of X

2.3.1. UV-vis spectra

All the cobaloximes exhibit an intense Co → dioxH CT band at ≈ 240 nm (Table 2). For the cobaloximes (**1b–5b**) the $\lambda_{\max}$ values fall in the following order, Cl > N₃ > CH₂Cl > Me ≈ Et. A similar trend was observed earlier for the dmgH complexes for Y = 3,5-lutidine and 2,6-dimethylpyrazine [24].

Furthermore, the $\lambda_{\max}$ values in (**1b–5b**) show a clear linear trend (discussed later) with the ¹³C of C=N_(oximinic) and the co-ordination shifts of ¹³C of Py_γ and ¹H of Py_α. However, for cobaloximes with triphenylphosphine (**1a–5a**) no clear correlation emerges.

2.3.2. ³¹P Chemical shifts

Phosphines and phosphites co-ordinated to cobalt(III) display a broad ³¹P peak due to a cobalt–phosphorus Fermi-contact interaction [42]. The ³¹P resonance of PPh₃ (−5.2δ) shifts downfield to 20–25δ when co-ordinated to the cobaloxime moiety. This is due to a large decrease in the electron density on the phosphorus (P → Co(dioxH)₂). In case of substituted phosphines, this co-ordination shift², has been found to depend on the phosphine cone angle [42]. Our results show that the nature of the *trans* ligand X also influences the Δ³¹P and it follows the order Cl > N₃ >

$$^2 \Delta^{31}\text{P} = {}^{31}\text{P}\delta_{\text{complex}} - {}^{31}\text{P}\delta_{\text{free}}.$$

$\text{CH}_2\text{Cl} > \text{Me} \approx \text{Et}$ (Table 3a). A similar trend was observed in the dmgh complexes with $\text{Y} = \text{Bu}_3\text{P}$ and $(\text{Bu}_3\text{O})_3\text{P}$ [42]. This similarity in the trend suggests that the *trans* influence order of X is independent of the dioxime moiety. The electronic *cis* influence of X in **(1a–5a)**³ is apparent from the following trends. $\Delta^{31}\text{P}$ shows a linear trend with ^{13}C resonance of the equatorial $\text{C}=\text{N}_{(\text{oximinic})}$ and C^2 carbons of the cyclohexane ring⁴.

$$\Delta^{31}\text{P} = 1.19 \delta^{13}\text{C}(\text{C}=\text{N})$$

$$- 152.04 \quad (r^2 = 0.94, \text{e.s.d.} = 0.74 \text{ ppm})$$

$$\Delta^{31}\text{P} = 5.05 \delta^{13}\text{C}(\text{C}^2)$$

$$- 101.70 \quad (r^2 = 0.91, \text{e.s.d.} = 0.86 \text{ ppm})$$

However, no correlation is observed between $\Delta^{31}\text{P}$ and the λ_{max} of $\text{Co} \rightarrow \text{dioxH}$ (MLCT).

2.3.3. ^{13}C Chemical shifts

The ^{13}C resonance of pyridine on co-ordination to the cobaloxime moiety shifts downfield by a few ppm and this co-ordination shift⁵ follows the order $\Delta^{13}\text{CPy}_\gamma > \Delta^{13}\text{CPy}_\beta > \Delta^{13}\text{CPy}_\alpha$ (Table 3b).

The *cis* and *trans* influence of the ligand X in **(1b–5b)** can be followed by $\Delta^{13}\text{C}$ values of pyridine and ^{13}C resonance of $\text{C}=\text{N}_{(\text{oximinic})}$. It follows the order $\text{Cl} > \text{N}_3 > \text{CH}_2\text{Cl} > \text{Me} \approx \text{Et}$ (Table 3a,b). The same trend was observed in $\Delta^{31}\text{P}$ and λ_{max} of $\text{Co} \rightarrow \text{dioxH}$ (MLCT) as mentioned earlier. It is also noticed that $\delta\text{C}=\text{N}$ in **(1a–5a)** show an upfield shift as compared to **(1b–5b)** indicating a higher charge density on $\text{C}=\text{N}$ in the former (Table 3a).

The co-ordination shift of the γ carbon of pyridine, $\Delta^{13}\text{CPy}_\gamma$, with variation in X correlates well with the λ_{max} of $\text{Co} \rightarrow \text{dioxH}$ (MLCT) as well as with the ^{13}C of $\text{C}=\text{N}_{(\text{oximinic})}$ indicating a similar origin of the *cis* influencing ability of X.

$$\lambda_{\text{max}} = 5.94\Delta^{13}\text{CPy}_\gamma$$

$$+ 237.7 \quad (r^2 = 0.91, \text{e.s.d.} = 1.73 \text{ nm})$$

$$\delta^{13}\text{C}(\text{C}=\text{N})$$

$$= 2.13\Delta^{13}\text{CPy}_\gamma + 146.98 \quad (r^2 = 0.99, \text{e.s.d.} = 0.17 \text{ ppm})$$

The co-ordination shift of β as well as α carbon of pyridine also show a linear trend with the ^{13}C of $\text{C}=\text{N}_{(\text{oximinic})}$.

$$\delta^{13}\text{C}(\text{C}=\text{N})$$

$$= 5.18\Delta^{13}\text{CPy}_\beta + 143.07 \quad (r^2 = 0.93, \text{e.s.d.} = 0.51 \text{ ppm})$$

$$\delta^{13}\text{C}(\text{C}=\text{N})$$

$$= 2.47\Delta^{13}\text{CPy}_\alpha + 149.94 \quad (r^2 = 0.95, \text{e.s.d.} = 0.42 \text{ ppm})$$

A good correlation is observed when ^{13}C of $\text{C}=\text{N}_{(\text{oximinic})}$ in **(1a–5a)** is compared with **(1b–5b)**

$$\delta^{13}\text{C}(\text{C}=\text{N}) \text{ PPh}_3$$

$$= 1.18\delta^{13}\text{C}(\text{C}=\text{N})\text{Py}$$

$$- 27.22 \quad (r^2 = 0.99, \text{e.s.d.} = 0.18 \text{ ppm})$$

2.3.4. ^1H Chemical shifts

The coordination shift of pyridine protons follow the order $\Delta^1\text{HPy}_\alpha < \Delta^1\text{HPy}_\beta < \Delta^1\text{HPy}_\gamma$ (Table 2) and shows that there is a increasing order of downfield shift from α to γ . However, only α protons show a clear trend in $\Delta^1\text{H}$. The *trans* influence of the X group on $^1\text{H}_\alpha$ can be followed by the co-ordination shift⁶ of the ligating pyridine and it follows $\text{Cl} > \text{N}_3 > \text{CH}_2\text{Cl} > \text{Me} \approx \text{Et}$ (Table 2). This order is similar to the one observed earlier for λ_{max} of $\text{Co} \rightarrow \text{dioxH}$ (MLCT), ^{31}P of PPh_3 , ^{13}C of Py_γ and of $\text{C}=\text{N}_{(\text{oximinic})}$.

The $\Delta^1\text{HPy}_\alpha$ has a linear variation with λ_{max} of $\text{Co} \rightarrow \text{dioxH}$ (MLCT) and ^{13}C of $\text{C}=\text{N}_{(\text{oximinic})}$. The least square equations obtained in the correlation are

$$\lambda_{\text{max}} = -27.37(630)\Delta^1\text{HPy}_\alpha$$

$$+ 248.03 \quad (114) \quad (r^2 = 0.91, \text{e.s.d.} = 2.16 \text{ nm})$$

$$\delta^{13}\text{C}(\text{C}=\text{N}) = 2.47(31)\Delta^1\text{HPy}_\alpha$$

$$+ 149.94 \quad (28)$$

$$(r^2 = 0.96, \text{e.s.d.} = 0.42 \text{ ppm})$$

Similar trends are observed for gH, dmgh and dpgh cobaloximes [24, 60c]. However, it is not possible to do correlation studies in complexes **(1a–5a)** because of the difficulty in assigning all the protons.

2.4. *Cis* and *trans* influence of the equatorial dioximes

In view of our recent study on the *cis* influence in organocobaloximes [46, 61–63], the present data allows us to extend our earlier conclusions further. The extent of electron density on the $\text{Co}(\text{dioxH})_2$ chelate ring for different dioximes (X and Y held constant) can be understood by comparing the ^{13}C chemical shifts of $(\text{C}=\text{N})$ of the equatorial dioxime, for example, for X = Me, Et or Cl and Y = Py it follows the order $\text{gH} < \text{dmgh} < \text{chgH} < \text{dpgh}$ (Table 4).

The *cis* influence of the dioximes on the axial ligands can also be followed by the co-ordination shifts of the α protons of pyridine ($\Delta^1\text{HPy}_\alpha$) and the ^1H resonance of the axial group (Table 4). For ΔPy_α the order is $\text{dmgh} \approx \text{chgH} < \text{gH} < \text{dpgh}$ (this order is based on the

³ The steric bulk of X is almost similar.

⁴ For numbering of carbons in the cyclohexane rings see Ref. [61].

⁵ $\Delta^{13}\text{C} = {}^{13}\text{C}\delta_{\text{complex}} - {}^{13}\text{C}\delta_{\text{free}}$.

⁶ $\Delta^1\text{H} = {}^1\text{H}\delta_{\text{complex}} - {}^1\text{H}\delta_{\text{free}}$.

values for X = Cl, Me, Et)⁷ and the *cis* influence order on the axial X group is $\text{dmgH} \approx \text{chgH} < \text{gH} < \text{dpgH}$ (this order is based on the (C_α) values for X = Me, Et)

The study shows that the *cis* influence of the equatorial oximes on the axial alkyl group is inter-related as evinced by the near ideal value of r^2 i.e. there is a good correlation of chgH complexes with other equatorial

Table 4

¹H shifts of Py_α , X and ¹³C shifts of C=N in different glyoximes

X	dioxH					
			GH	dmgH	chgH	dpgH
Cl	¹ H	Py_α	8.28 ^a	8.25	8.26 ^b	8.62 ^c
		ΔPy_α	−0.29	−0.32	−0.31	0.05
	¹³ C	C=N	140.56 ^c	152.59	153.62	153.69
N ₃	¹ H	Py_α			8.32 ^b	
		ΔPy_α			−0.25	
	¹³ C	C=N		152.11	153.12	
ClCH ₂	¹ H	Py_α			8.58 ^b	
		ΔPy_α			0.01	
		CH ₂			3.78	
	¹³ C	C=N			151.12	
Me	¹ H	Py_α	8.67 ^a	8.59	8.62 ^b	9.00 ^a
		ΔPy_α	0.10	0.02	0.05	0.43
		CH ₃	1.02	0.82	0.85	1.44
	¹³ C	C=N	138.10 ^c	149.89	150.04	150.90
Et	¹ H	Py_α	8.67 ^a	8.56 ^d	8.6 ^c	8.87 ^d
		ΔPy_α	0.10	0.01	0.03	0.3
		CH ₂	1.9	1.74	1.74	2.35
		CH ₃	0.53	0.35	0.37	0.81
	¹³ C	C=N	138.81 ^c	149.92	150.07	150.85

^a Ref. [55].

^b This study.

^c Ref. [59].

^d Ref. [61].

^e From our lab, unpublished work.

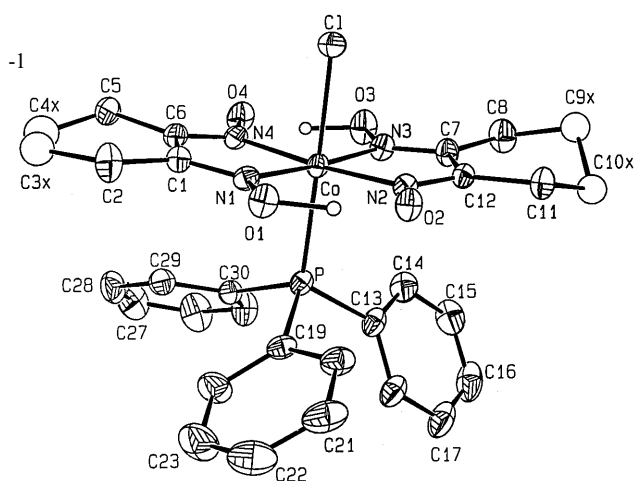


Fig. 1. ORTEP plot of structure $\text{ClCo}(\text{chgH})_2\text{PPh}_3$ (**1a**).

⁷ Others can not be compared since the data for all the four sets of dioximes is not available.

oxime complexes (based on ¹H chemical shifts of axial group).

$$\delta^1\text{H}_{\text{chgH}} = 1.00(0) \delta^1\text{H}_{\text{gH}} - 0.16(0) (r^2 = 0.99, \text{e.s.d.} = 0.00 \text{ ppm})$$

$$\delta^1\text{H}_{\text{chgH}} = 0.98(1) \delta^1\text{H}_{\text{dmgH}} + 0.03(1) (r^2 = 0.99, \text{e.s.d.} = 0.01 \text{ ppm})$$

$$\delta^1\text{H}_{\text{chgH}} = 0.90(6) \delta^1\text{H}_{\text{dpgH}} - 0.39(9) (r^2 = 0.99, \text{e.s.d.} = 0.06 \text{ ppm})$$

2.4.1. X-ray crystal structure

Dark brown crystals of $\text{ClCo}(\text{chgH})_2\text{PPh}_3$ (**1a**) was grown from methanol and was subjected to X-ray crystallography. The ORTEP plot of **1a** is shown in Fig. 1. Pertinent crystal data and refinement parameters and interatomic distances are compiled in Tables 5 and 6.

Both cyclohexane rings have disorder in the two outer carbon positions. It was modelled with split carbons, which were refined isotropically. The C₃–C₄ disorder is 50–50 in occupancy in the model, and seems to indicate a disorder with both C's either above or below the general plane of the ring. The C₉–C₁₀ disorder was 60–40 occupancy, and seems to indicate a twist disorder with the bonded pairs each having one atom above and one atom below. This arrangement appears to model the disorder fairly well but some of the bond lengths and angles involved with these atoms suggest that the real situation is perhaps not quite this simple. The H atoms for the OH groups were located on difference maps and were restrained to those difference map positions.

A comparative study (Table 7) of the bond angles and bond lengths in compound $\text{ClCo}(\text{chgH})_2(\text{PPh}_3)$ (**1a**) with that of $\text{ClCo}(\text{dmgH})_2(\text{PPh}_3)$ [68], the closest structure for comparison, shows that the Co–P and Co–Cl bond length does not change with the change in the equatorial ligand. The cobalt atom in compound **1a** is 0.0742(19) Å out of the mean plane of the four nitrogen atoms that is nearly the same as in the dmgH complex (0.05 Å). The bulk of the chgH wings manifests itself in the increased α value [11.3(3)°] for the chgH complex as compared to the dmgH complex [6°]. A similar increase is observed when the gH complex is compared with the dmgH complex (Table 7) confirming that the increase in equatorial bulk leads to an increase in α value.

3. Conclusions

The study highlights that a change in X leads to a systematic variation in the spectroscopic properties in the dioxime ligands and in the axial ligand Y and the *trans* influence order of X is independent of the dioxime moiety. A systematic change in the steric and electronic

Table 5
Crystal data collection and refinement parameters

Formula	C ₃₀ H ₃₃ ClCoN ₄ O ₄ P
Formula weight	638.97
Crystal size (mm)	0.30 × 0.34 × 0.36
Crystal color	Brown
Crystal mount	On glass fiber with silicone glue
<i>a</i> (Å)	11.058(2)
<i>b</i> (Å)	15.310(2)
<i>c</i> (Å)	17.3122(18)
β (°)	92.465(12)
<i>V</i> (Å ³)	2928.1(7)
Cell detn, reflections	25
Cell detn, 2θ range (°)	20–21
<i>D</i> _{calc} (g cm ^{−3})	1.45
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4
<i>F</i> (000)	1330.6
Radiation	Mo–K α , graphite monochromated
λ (Å)	0.7107
Temperature (K)	293
Linear absorption coefficient (mm ^{−1})	0.77
Diffractometer	Enraf–Nonius CAD-4
Scan technique	θ – 2θ
Scan width (°)	1.0 + 0.35 tan θ
2θ range (°)	4–50
<i>h,k,l</i> ranges	−13, 13; 0, 18; 0, 20
Standard reflection indices	1, 1, 3; 4, 0, 6; −4, 1, 6
Drift of stds (%)	0.5
Absorption correction	Analytical
Absorption range	0.75–0.82
Reflections measured	5313
Unique reflections	5135
<i>R</i> for merge	0.022
Reflections in refinement	3627
[<i>I</i> > 1.0 σ (<i>I</i>)]	
Solution method	Direct methods
Parameters refined	367
<i>R</i> (<i>F</i>), <i>R</i> <i>w</i> (<i>F</i>)	0.052, 0.057
<i>R</i> for <i>I</i> > 3.0 σ (<i>I</i>)	0.041
Goodness-of-fit	1.18
<i>p</i> , <i>w</i> ^{−1} = [<i>I</i> ² + <i>pI</i> ²]/4 <i>F</i> ²	0.03
Largest Δ	0.00
Extinction correction ^b	0.61(9)
Final difference map, (e Å ^{−3})	−0.42(8), +0.38(8)
Programs	NRC386 (PC version of NRCVAX) ^a
Scattering factors	International Tables for Crystallography, vol 4
H atom treatment	Idealized (C–H = 0.95 Å)

^a NRCVAX — An Interactive Program System for Structure Analysis, E.J. Gabe, Y. Lepage, J.P. Charland, F.L. Lee, and P.S. White, J. Appl. Cryst. 22, 383 (1989).

^b Larson, A.C. Crystallographic Computing, Munksgaard Copenhagen 293 (1970).

properties of the dioxime moiety also manifests its *cis* influence on the spectroscopic properties of the axial ligands.

As progressively more spectroscopic, equilibrium and structural data on the cobaloximes with various dioximes like gH, chgH and dpghH accumulate, the

Table 6
Interatomic distances (Å) and angles (°)

Co–Cl	2.2771(13)	Co–P	2.3222(13)
Co–N1	1.894(3)	Co–N2	1.896(3)
Co–N3	1.883(4)	Co–N4	1.892(3)
P–C13	1.836(5)	P–C19	1.829(4)
P–C30	1.828(4)	O1–N1	1.351(4)
O1–Ho1	1.188(3)	O2–N2	1.336(4)
O3–N3	1.349(4)	O3–Ho3	1.172(3)
O4–N4	1.344(5)	N1–C1	1.299(6)
N2–C12	1.291(6)	N3–C7	1.292(6)
N4–C6	1.294(6)	C1–C2	1.482(7)
C1–C6	1.443(6)	C2–C3x	1.532(13)
C2–C3y	1.469(14)	C3x–C4x	1.338(18)
C3y–C4y	1.331(18)	C4x–C5	1.469(14)
C4y–C5	1.576(13)	C5–C6	1.504(6)
C7–C8	1.497(7)	C7–C12	1.458(6)
C8–C9x	1.567(11)	C8–C9y	1.474(15)
C9x–C10x	1.522(13)	C9y–C10y	1.51(2)
C10x–C11	1.521(10)	C10y–C11	1.542(15)
C11–C12	1.497(6)	C13–C14	1.404(8)
C13–C18	1.392(7)	C14–C15	1.379(8)
C15–C16	1.380(11)	C16–C17	1.370(11)
C17–C18	1.379(8)	C19–C20	1.390(6)
C19–C24	1.382(7)	C20–C21	1.391(7)
C21–C22	1.374(10)	C22–C23	1.347(10)
C23–C24	1.394(7)	C25–C26	1.384(7)
C25–C30	1.380(7)	C26–C27	1.371(10)
C27–C28	1.366(9)	C28–C29	1.395(7)
C29–C30	1.386(7)		
Cl–Co–P	177.80(5)	Cl–Co–N	188.20(11)
Cl–Co–N2	87.14(11)	Cl–Co–N3	87.82(12)
Cl–Co–N4	87.84(11)	P–Co–N1	89.73(11)
P–Co–N2	92.42(11)	P–Co–N3	94.25(12)
P–Co–N4	92.60(11)	N1–Co–N2	98.37(15)
N1–Co–N3	176.01(15)	N1–Co–N4	81.64(15)
N2–Co–N3	81.78(15)	N2–Co–N4	174.98(15)
N3–Co–N4	97.87(15)	Co–P–C13	117.07(16)
Co–P–C19	111.83(15)	Co–P–C30	113.41(14)
C13–P–C19	103.7(2)	C13–P–C30	103.4(2)
C19–P–C30	106.3(2)	N1–O1–Ho1	107.4(3)
N3–O3–Ho3	101.9(3)	Co–N1–O1	123.5(3)
Co–N1–C1	115.5(3)	O1–N1–C1	120.8(4)
Co–N2–O2	122.8(3)	Co–N2–C12	115.5(3)
O2–N2–C12	121.3(3)	Co–N3–O3	124.2(3)
Co–N3–C7	116.3(3)	O3–N3–C7	119.4(4)
Co–N4–O4	122.6(3)	Co–N4–C6	115.9(3)
O4–N4–C6	121.3(3)	N1–C1–C2	124.2(4)
N1–C1–C6	113.6(4)	C2–C1–C6	122.3(4)
C1–C2–C3x	111.5(6)	C1–C2–C3y	111.2(7)
C2–C3x–C4x	124.5(10)	C2–C3y–C4y	126.1(11)
C3x–C4x–C5	123.7(11)	C3y–C4y–C5	121.5(10)
C4x–C5–C6	111.7(6)	C4y–C5–C6	110.8(6)
N4–C6–C1	113.3(4)	N4–C6–C5	124.4(4)
C1–C6–C5	122.3(4)	N3–C7–C8	125.3(4)
N3–C7–C12	112.8(4)	C8–C7–C12	121.9(4)
C7–C8–C9x	110.0(5)	C7–C8–C9y	114.4(6)
C8–C9x–C10x	110.9(7)	C8–C9y–C10y	110.4(11)
C9x–C10x–C11	106.9(7)	C9y–C10y–C11	114.5(11)
C10x–C11–C12	112.2(5)	C10y–C11–C12	110.5(6)
N2–C12–C7	113.6(4)	N2–C12–C11	125.0(4)
C7–C12–C11	121.3(4)	P–C13–C14	120.7(4)
P–C13–C18	120.3(4)	C14–C13–C18	118.6(4)
C13–C14–C15	120.3(5)	C14–C15–C16	120.2(6)
C15–C16–C17	119.7(5)	C16–C17–C18	121.2(6)

Table 6 (Continued)

C13–C18–C17	119.9(5)	P–C19–C20	118.6(4)
P–C19–C24	122.8(3)	C20–C19–C24	118.5(4)
C19–C20–C21	120.2(5)	C20–C21–C22	120.4(5)
C21–C22–C23	119.6(5)	C22–C23–C24	121.2(6)
C19–C24–C23	120.0(5)	C26–C25–C30	120.9(5)
C25–C26–C27	119.9(5)	C26–C27–C28	120.4(5)
C27–C28–C29	119.7(5)	C28–C29–C30	120.6(5)
P–C30–C25	120.8(4)	P–C30–C29	120.8(3)
C25–C30–C29	118.4(4)		

generalities of the correlations, initially observed in the dmgh complexes, can be tested further in future.

4. Experimental

Cobalt(II) chloride hexahydrate, cobalt acetate tetrahydrate, sodium azide, 1,2 cyclohexanedionedioxime, pyridine, triphenylphosphine, methyl iodide and ethyl iodide were obtained from commercial sources (Fluka AG) and were used as such without further purification. All solvents were distilled prior to use.

¹H-NMR (400 MHz, CDCl₃, Int. Std. TMS), ¹³C-NMR (100 MHz, CDCl₃) and ³¹P (162.7 MHz, Ext. Std. H₃PO₄) were recorded on a JOEL LA-400 Spectrometer. UV–vis spectra were recorded on a Shimadzu 160-A Spectrophotometer in chloroform. X-ray studies were done on Enraf Nonius CAD-4 diffractometer at Fayetteville, Arkansas, USA.

4.1. Synthesis of ClCo(chgH)₂Py

Method (1a) Pyridine (0.14 gm, 1.75 mmol) was added with constant stirring to a refluxing solution of cobalt(II) chloride hexahydrate (0.41 g, 1.75 mmol) and 1,2 cyclohexanedionedioxime (0.50 g, 3.51 mmol) in

95% ethanol (25 ml). The solution was allowed to cool to r.t. and air was passed through the reaction mixture for 6 h. The dark brown precipitate was filtered, washed with ethanol (2 × 3 ml), ether (2 × 3 ml), dried and purified by column chromatography.

(1b) Cobalt chloride hexahydrate (0.74 g, 3.10 mmol) was dissolved in acetone (40 ml) and 1,2 cyclohexanedionedioxime (1.00 g, 7.03 mmol) was added with constant stirring. The reddish orange coloured mixture was stirred for 0.5 h and pyridine (0.58 g, 7.36 mmol) was added dropwise. The colour of the reaction mixture immediately turned brown and then slowly changed to green. After overnight stirring, a brown precipitate appeared which was filtered, washed with acetone (2 × 3 ml), ether (2 × 3 ml), dried and purified by column chromatography.

Synthesis of ClCo(chgH)₂PPh₃: The same procedure was used as above but triphenylphosphine was used instead of pyridine.

4.2. Synthesis of N₃Co(chgH)₂Py

Method (2a) Pyridine (0.267 gm, 3.37 mmol) was added with constant stirring to a refluxing solution of cobalt(II) acetate tetrahydrate (0.39 g, 1.59 mmol), 1,2 cyclohexanedionedioxime (0.50 g, 3.51 mmol) in 95% ethanol (25.0 ml) followed by sodium azide (0.103 g, 1.58 mmol). The solution was allowed to cool to r.t. and air was passed through the reaction mixture for 3 h. The dark brown precipitate was filtered, washed with ethanol (2 × 2.5 ml) dried and purified by column chromatography.

Half the amount of pyridine or triphenylphosphine used in the above methods (method 1a,b and 2a) can be replaced with NaOH or KOH.

(2b) Sodium azide (0.065 gm, 1.00 mmol) dissolved in 5 ml water was added to a refluxing suspension of ClCo(chgH)₂Py (0.400 g, 0.87 mmol) in 50.0 ml methanol. The reaction mixture was further refluxed for 2 h and the volume reduced to 10 ml by rotary evaporator. The red–brown solid was filtered, washed with methanol (2 × 2.5 ml), pet ether (2 × 3.0 ml), dried and purified by column chromatography.

4.3. Synthesis of N₃Co(chgH)₂PPh₃

The same procedure as outlined above was used but triphenylphosphine was used instead of pyridine.

4.4. Synthesis of XCo(chgH)₂Y; (X = Me, Et, ClCH₂; Y = Py, PPh₃)

These were prepared by following the procedure reported earlier by us [61].

Table 7
Comparison of bond lengths and bond angles of XCo(L)₂PPh₃^a

L=X=	dmgh [68] Cl	chgH ^b Cl	gH [55] Me	dmgh [55,69] Me
Co–P	2.327(4)	2.3222(13)	2.428(1)	2.418(1)
Co–X	2.277(4)	2.2771(13)	2.033(3)	2.026(6)
α	6	11.3(3)	6	11
D	0.050	0.0742(19)	0.11	0.11
Co–N _{eq}	1.89(1)	1.89(3)	1.883(2)	1.891(5)
N ₁ –Co–N ₁	98.7(2)	98.12(15)	97.7(1)	98.0(2)
N ₁ –Co–N ₂	81.3(5)	81.71(15)	82.0(1)	81.7(2)
Co–N–C _{ox}		115.8(3)	115.8(2)	116.5(4)
N–C _{ox} –C'		124.7(4)		122.7(6)
N–Cox–Cox		113.3(6)	113.3(3)	112.7

^a Bond angles (°) and bond lengths (Å).

^b This study.

4.5. Purification by column chromatography

All the complexes were purified using a silica gel column 100–200 mesh using chloroform–ethylacetate as the eluent.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 137919 for compound **1a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +4-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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